#### Monitoring and Laboratory Division Air Quality Surveillance Branch

#### Sampling Protocol for Acrolein Application Pilot Study

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Prepared by:

Jack Romans Air Pollution Specialist Special Purpose Monitoring Section

Signatures:

7-28-05 Kenneth R. Stroud, Chief

Air Quality Surveillance Branch

Air Resources Board

Mike Poore, Chief

Date

Northern Laboratory Branch

Air Resources Board

The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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#### 1.0 Background

DPR's (California Department of Pesticide Regulation) Draft Report dated January 2005, "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredients Acrolein", recommends that the Air Resources Board (ARB) conduct a comprehensive air monitoring study for Acrolein during a field application.

Before proceeding with a full-scale study, ARB's Monitoring and Laboratory Division (MLD) suggests a pilot study to determine the applicability of the proposed field test method. A limited number of ambient air samples will be collected during an application. Laboratory analysis of these samples will confirm the applicability of the proposed field test method for use in the full-scale study.

An Acrolein application pilot study was subsequently approved by DPR.

#### 2.0 Project Goal and Objectives

The primary goal of this monitoring project is to measure the concentrations of acrolein in the ambient air during an application. Secondary goals include the determination of what sampling and analytical methods are suitable for future air sampling during acrolein applications.

To achieve the project's goal, the following objectives should be met:

- Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.
- 2. Appropriate application of sampling/monitoring equipment to determine ambient acrolein concentrations.
- 3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.
- 4. Determination of suitability of applied sampling and analytical methods.
- 5. At the conclusion of the project, MLD to provide DPR with a draft report or memorandum containing all relevant information, data and results gathered in the course of MLD's activities during the planning and execution of this project. If available, electronic versions of these documents, data and results will also be included.

#### 3.0 Contacts, Roles and Responsibilities

Peter Ouchida, Manager Special Purpose Monitoring Section 916-322-3719

Jack Romans, Field Monitoring Project Lead Special Purpose Monitoring Section Office – 916-327-4716 Cell – 916-952-9520

Andy Cowell, Field Monitoring Project Technician Special Purpose Monitoring Section
Office – 916-445-1043 Cell – 916-952-5447

Kathleen Gill, Manager Organics Laboratory Section 445-9483

Lynn Baker, Staff Air Pollution Specialist Stationary Source Division 916-324-6997

Randy Segawa, Senior Environmental Research Scientist Department of Pesticide Regulation 324-4137

#### 4.0 Study Location

An acrolein application is planned for August 3, 2005, at canal owned an operated by the Kern Delta Water District in Bakersfield, CA.

#### 5.0 Study Design

- a) Five separate sampling sites will surround the application area. Sites will be positioned according to wind direction prevalent and expected at the time of application to provide at least one upwind and one downwind site. Since application is into a water body (canal), both sides of the canal will have samplers in keeping with these other requirements. Sampling sites will generally be less than approximately 20 meters distant from point of application as well as canal depending on safety and logistical constraints. A portable meteorological station measuring wind speed and direction, outdoor temperature and relative humidity, will be located on or within this perimeter.
- b) Each sampling site will have at least one air sampler. The air sampler will consist of an evacuated Acculife-treated stainless-steel canister (6 liters capacity) drawing ambient air through a Restek Veriflo SC424XL passive flow controller. The air sample will be collected at breathing-level (approximately 2 meters above the ground) using a 1/8-inch diameter and 2 meters long treated stainless-steel sample probe. The sample collection period will be integrated over a time period that is most nearly coincident with the application period. Depending on the installed orifice, the flow controller can integrate, 1-hour (40-80 ml/min), 3-hour (20-40 ml/min), 8-hour (8-20 ml/min), 12-hour, or 24-hour samples. It is anticipated that a 3-hour sample will be collected.
- c) At the start of the application, sample collection will be initiated by simultaneously opening all canister-valves. At the end of the application period, all valves will be simultaneously closed, flow controllers removed, and canisters transported to the lab for analysis. Field notes will be made of field and application descriptions, sampling data and all observations that may pertain to the study.
- (d) Meteorological data will be collected using one Met One Instruments' AutoMet Digital Meteorological Monitoring System located within the sampling perimeter. The height of the Met sensors above the ground is approximately 3 meters. The meteorological station will continuously measure and record 1-minute averages of ambient temperature, wind speed, wind direction, and relative humidity throughout the duration of the application period.
- (e) Following the conclusion of the application, MLD will provide DPR with a draft report or memorandum containing all relevant information, collected data and analytical results gathered during the course of the study. If available, electronic versions of the aforementioned will also be provided.
- (f) Table 1 lists Siting Criteria referenced from ARB's Quality Assurance Manual, Volume II. The listed criteria are identical to those contained in the Quality Assurance Plan for Pesticide Monitoring except for the latter does not include a requirement for sampler distance from roadway and traffic.

#### 5.0 Study Design (continued)

Table 1

#### Siting Criteria\*

Item/ Influence	Requirements				
Height of Sample Inlet	2 to 7 meters above the ground				
Spacing Between Inlets (Collocated)	Within 4 meters, but at least 1 meter apart.				
Obstacles	Distance between samplers and obstacles must				
	be at least 2 times the height the obstacle protrudes above the sampler.				
Tree Dripline	Inlet must be at least 10 meters from dripline if tree represents an obstruction.				
Walls, Parapets, etc.	Inlet must be 2 meters from walls, parapets, etc.				
Air Flow Arc	Unrestricted 270 degree arc that must include				
	predominant wind direction for seasonal high pollutant; samplers located on the side of a building				
	require 180-degree clearance.				
Traffic	ffic No specific requirement for pesticide monitoring				

<sup>\*</sup>From 40 CFR Part 58, Appendix E, and ARB Quality Assurance Manual, Vol. II, section 2.0.4 (Feb. 2000)

#### 6.0 Sampling Methodology

The Northern Laboratory Branch (NLB) will supply SPM with six (6) evacuated treated stainless-steel canisters with individual shipping/protective boxes. A field sample report/chain-of-custody form (Figure 1) initiated by the lab will accompany each canister. NLB will perform analyses for acrolein on all collected samples and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (SOP MLD 066), "Standard Operating Procedures for the Analysis of Oxygenated and Nitrile Hydrocarbons in Ambient Air Using Summa Canister Sampling and Gas Chromatographic/Mass Spectrometric Analysis". This analytical method currently has a Level of Detection (LOD) of 0.3 ppbv (0.6 micrograms per cubic meter). SOP MLD 066 is included in this Protocol as Appendix A.

Staff of the Special Purpose Monitoring Section (SPM) will hand-carry canisters to and from MLD's laboratory in Sacramento and to and from the sampling location. The canisters will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample.

#### 6.0 Sampling Methodology (continued)

At each sampling site, the operator will assure that the canister valve is closed and record prerun information on field sample report. The passive flow controller with sample probe will then be attached to the canister. At the start of the application, the valves of all canisters (except the spare) will be simultaneously opened and the time and beginning vacuum reading recorded. The valves will be simultaneously closed when one of the following conditions is met (whichever occurs first):

- a) At the end of the application period.
- b) At the end of the 3-hour sampling period.
- c) When the canister gauge reads a vacuum of -5 inches of Hg.

Post-run information will be recorded on field sample report.

Sampling will occur as scheduled unless meteorological conditions at the start of application are either rain or if instantaneous wind speeds gusts are over 10 knots/miles per hour.

All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

#### 6.0 List of Field Equipment

#### Quantity

#### Item Description

- (1) Met-One Automet portable meteorology system having sensors for measuring wind speed and direction, ambient temperature, and relative humidity w/built-in data logger.
- (6) Evacuated stainless-steel canister, each equipped with a vacuum/pressure gauge and a field data sheet/report (4 ambient canisters plus 2 collocated canisters).
- (6) Restek passive flow controller equipped with 3-hour orifice.
- (6) 2 meters long, 1/8-inch diameter, treated stainless-steel sample probe.
- (6) Concrete pier for mounting air sampler.

Various equipment for calibrating and setting-up meteorological station.

Various equipment for measuring and documenting application parameters.

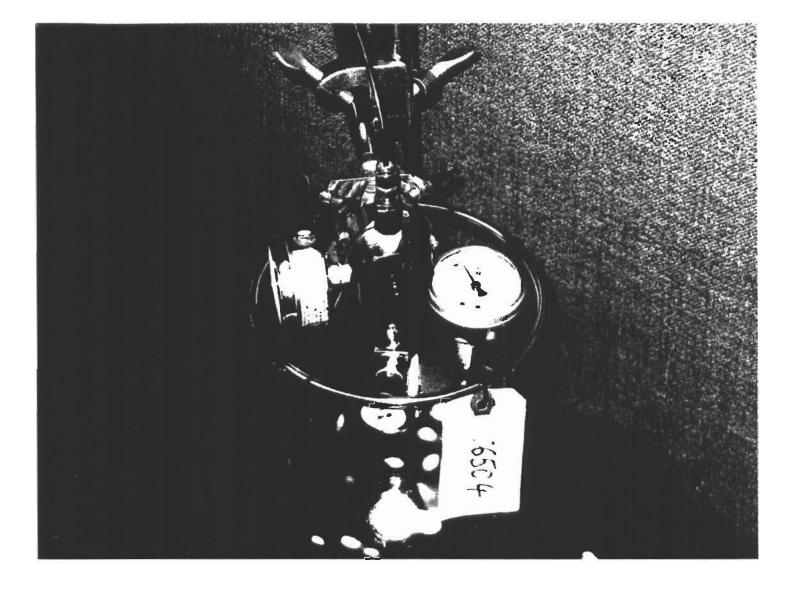


Figure 1

Air Sampler – Canister with Passive Flow Controller

# Figure 2 Field Sample with Chain of Custody Report

[Please place data sheet inside plastic pouch]

#### **CALIFORNIA AIR RESOURCES BOARD**

### **Xontech 910A Toxics Data Sheet/Sample Tracking**

Site Name:						Sit€
Station Operator/Agency:						Scheduled
Project Name (If Applicable):						
					CANIST	TER
		T				
	Date	Time (PST)		:uum Hg)		Pressure (PSI)
·			LAB	FIELD		
Set-Up						
Start						
					FIELD	LAB I
Stop	J		HAVE .			
Type of Sample:		[ ] Re	egular	[	] Colloca	-
Canister ID Number:						Air Samp
Observed Unusual Sampling Condition:			Wind-B Constru		and/Dust earby	[ ] Rain [ ] Fire
	INV	ALID SA	MPLE	NFOR	MATION	
Reason for Sample Invalidation						
[ ] Low canister pressure [ ] High canister pressure						[
[ ] Sampling period out of range (<23 or >25 hours)						[
[ ] Sampling equipment inoperative [ ] Damaged sampling media						į.
[ ] Lab unable to provide sample media						
[ ] Other reasons:						
Field Comments:						
		Sample	Tracki	ng		
Action			er Method ck one) Person			Name & Ir

#### 8.0 Quality Assurance/Quality Control

Quality assurance and quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the passive flow controllers will be measured using a mass flow meter having a current calibration certification and a range of 0-100 cubic centimeters per minute.

The following certified transfer standards and equipment will be used to calibrate and align the meteorological sensors:

TEMPERATURE	RELATIVE HUMIDITY	WIND DIRECTION	WIND SPEED
DIGISENSR RTD DATALOGGER Model No. 93410-50	Rotronic EA10 Salt Std.  " EA35 " "  EA50 " "  EA 80 " "	BRUNTON Model 5008 Pocket Transit	RM Young Model 18111 Anemometer Drive
		RM Young Model 18310 Torque Disk	
		Met-One 040 Degree Fixture	

Each sample canister will be assigned a field sample report (Figure 1) that provides for identification of site, sampler, operator, and sample information as well as sample chain-of-custody transfer information.

Collocated (side-by-side) air samplers will operate at two sites during the application period. These collocated sites will be the ones with the highest expected concentrations (downwind).

#### 9.0 Deliverables

Following completion of field monitoring, MLD will provide DPR with a draft report/memorandum containing or covering the following sections:

- 1) Sampling Protocol
- 2) Personnel Contact List
- 3) Site Maps
- 4) Site Photographs
- 5) Site Descriptions and Measurements (site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments)
- 6) Sample Summary Table
- 7) Field Sample/Chain of Custody Reports
- 8) Laboratory Analysis Reports w/calculations in electronic (preferred) format if available
- 9) Met Station and Sampler Calibration Reports
- 10) Transfer Standards' Certification Reports
- 11) Floppy Disk containing electronic files of 1-minute averages of Meteorological Data
- 12) Floppy Disk containing electronic files of Draft Report

In addition, the Special Purpose Monitoring Section will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

## Appendix A: STANDARD OPERATING PROCEDURE, SAMPLING AND ANALYSIS OF ACROLEIN IN SILCO CANISTERS

The Organics Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for acrolein collected by the canister method. This analytical procedure is entitled, "Standard Operating Procedure for the Determination of Oxygenates and Nitriles in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" and may be found in its entirety at: <a href="http://www.arb.ca.gov/aaqm/sop/sop\_066.pdf">http://www.arb.ca.gov/aaqm/sop/sop\_066.pdf</a>